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SULFUR FIXATION OF COAL FINE AGGLOMERATES IN THE
PRESENCE OF LIMESTONE AT OXIDIZING ATMOSPHERE

by

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ABSTRACT

Utilization of coal fine agglomerates in the presence of limestone offers an advantage of in-situ sulfur fixation in the agglomerates during combustion and/or gasification to minimize the emission of SO_2 into the atmosphere. An experiment is carried out to study the kinetics of sulfur fixation in the coal fine-limestone agglomerates in air stream at temperature ranges of 500°C - 900°C using a fixed bed reactor. Seventy percent of total sulfur reaction in the agglomerates can be achieved with Ca/S mole ratio of 3. The rate of sulfur fixation, in terms of total sulfur and sulfate sulfur retained, in the coal fine agglomerates can be represented by a coupled diffusion and zone reaction model. The activation energy of the overall sulfur fixation reaction is found to be 4 - 7 Kcal/mole.

INTRODUCTION

The most serious environmental problems in coal mining regions are the coal fine slurry impoundments. They not only present hazardous conditions to the local communities, but also restrict the use of land and water resources. Because of current concern over the impending energy shortages and environmental problems, the coal fine wastes must be recovered from tailing impoundments and waste streams of processing plants. This can be used to clean up the coal slurry impoundments and avoid need for impoundments to protect our environment. A potentially attractive method to recover and utilize these coal fines in producing clean energy with in-situ sulfur fixation has been developed. The proposed flow sheet is depicted in Fig. 1.(1) This process includes coal fine-limestone agglomeration and combustion steps.

A number of publications have disclosed the effectiveness of applying sulfur acceptor sorbents within sulfide ore pellets for in-situ sulfur fixation and used as a hydrogen sulfide scavenger. (2,3) The sulfur dioxide was formed and adsorbed by sorbent within the pellets as a hydrate (CaSO_4) during air roasting ($\sim 500^\circ\text{C}$). The hydrate was insoluble in acids and the sulfur was retained in the pellets during the subsequent acid leaching process. On the other hand, the hydrogen sulfide was generated and accepted by sorbent within the pellets in H_2 or steam atmosphere (600°C - 800°C). The CaS in the pellets could be recovered as sulfur after the acid leaching process. Lime ($\text{Ca}(\text{OH})_2$) was the only common sorbent that would adequately control SO_2 or H_2S evolution within the sulfide ore pellets during the roasting or reduction processes. Approximately 90 percent of sulfur could be converted to CaS or CaSO_4 in the pellets in the presence of a stoichiometric amount of $\text{Ca}(\text{OH})_2$.

The processes related to the in-situ sulfur fixation in the coal pellets in the presence of limestone were reported by LaRosa and Michaels (4), Buttermore (5), and Ban, et al. (6) Sixteen percent sulfur content of Illinois coal refuse was mixed with limestone and carbonized in the N_2 atmosphere. Sixty-two percent of sulfur converted to CaS and FeS within the pellets was reported by LaRosa, et al. Buttermore investigated the effect of various sorbents on the Ohio raw coal and West Virginia coal refuse for sulfur fixation in the pellets. The results showed

that a 100% sulfur retention efficiency in coal hydrated lime pellets and 93% in the coal-limestone pellets at the 180% stoichiometric CaO could be achieved. A clean pellet fuel process was developed by Ban, et al. Approximately 95% sulfur was retained during carbonization and about 75% of original sulfur was retained in the pellets in the presence of limestone with Ca/S mole ratio of 3 during combustion.

No kinetic data on the in-situ sulfur fixation reaction in the coal fine-limestone agglomerates has been reported. Therefore, it is the aim of this investigation to obtain rate data and to formulate the rate expressions for prediction and interpretation of the phenomena. The information is important in process design and operations. The mathematical model is also useful to apply in preparing the high sulfur coal to generate the clean energy and in predicting the sulfur fixation by calcium (as mineral matter in coal) in coal during the combustion and/or gasification.

EXPERIMENTAL

The coal fines were collected from a 9 year old coal slurry impoundment. The coal fine tailing contained 41.6% ash, 25.6% volatile matter, 1.62% total sulfur and 18,575 KJ/Kg (7,683 BTU/lb). The sulfur forms included 0.88% organic sulfur, 0.11 pyritic sulfur, and 0.63% sulfate sulfur. The low temperature ash analysis showed there was 2.96% CaO content in the coal ash. The Greer limestone was used as a SO₂ acceptor which contained 45.15% CaO. The coal fine tailing and limestone (Ca/S mole ratio 0 - 4) in the size range of 140M x 200M (106 - 75µm) were blended with 15% water by wt. and balled in a glass tubing by hand. All experiments were performed in a 26mm ID x 120mm L quartz tube which was used as a fixed bed reactor. The schematic diagram of the experimental apparatus is shown in Fig. 2. In a typical experimental run, the agglomerates (~1 g) were placed in a 60 mesh stainless steel sample holder and loaded in the cooling zone, while the reactor was continuously purging with air flow rate of 2 l/min, and maintained at a desired reaction temperature 500°, 700° or 900°C. To start the experiment, the coal sample was slid into the hot zone for combustion. The sample was slid back to the cooling zone at predesigned combustion time, while the air stream was switched to N₂ gas. The weight loss of the agglomerates were determined and sulfur forms of the agglomerates were analyzed by ASTM standard methods.

KINETIC MODELING

In the coal fine-limestone agglomerates, the solid reactants are visualized as being composed of a large number of spherical limestone particles and coal fine particles with the sulfur imbedded in the coal particles. In the overall agglomerate, the agglomerate is porous, the gaseous reactant, O₂, diffuses easily through the interstices between coal fine and limestone particles, and through the product layers surrounding the solid reactant grains in the particles. The chemical reaction then proceeds according to zone reaction model (7) in individual particles. The model is schematically shown in Fig. 3. The sulfur fixation reactions in the coal fine-limestone agglomerates involve the successive multiple solid-gas reactions. Three major chemical reactions, which contribute to the sulfur fixation in the agglomerates, can be represented by the following reactions:



If the order of reactions, with respect to the individual reactant, are first order, and the concentration of gaseous intermediate, SO₂, is much less than that of gaseous reactant O₂, the rate of mass transport of SO₂ within the solid product layers will become rate controlling. Therefore, application of a coupled diffusion and zone reaction models can be used in describing the mass transfers in the particles and agglomerates, and the successive multiple reactions for calcium sulfate formation. The rate expressions are:

$$\frac{dx_1}{dt} = \frac{A K_1 x_{m1} (1 - \frac{x_1}{x_{m1}})^{2/3}}{1 + \frac{A \cdot K_1}{A \cdot D_1} (1 - \frac{x_1}{x_{m1}})^{1/3} (1 - (1 - \frac{x_1}{x_{m1}})^{1/3})} = R_1 \quad (4)$$

$$\frac{dx_2}{dt} = R_1 - R_2 \quad (5)$$

$$\frac{dx_3}{dt} = \frac{B x_{m3} K_2 (1 - \frac{x_3}{x_{m3}})^{2/3} x_2 x_4}{1 + \frac{B \cdot K_2}{B \cdot D_2} (1 - \frac{x_3}{x_{m3}})^{1/3} (1 - (1 - \frac{x_3}{x_{m3}})^{1/3})} = R_2$$

$$\frac{dx_4}{dt} = \frac{C D_3 (1 - x_4)^{1/3}}{1 - (1 - x_4)^{1/3}} \quad (7)$$

With the conditions:

$$\begin{aligned} x_1 = x_2 = x_3 = x_4 &= 0 & \text{at } t = 0 \\ (1 - x_1) + x_2 + x_3 &= 1.0 & \text{at } t > 0 \end{aligned}$$

The rate expressions can be numerically analyzed by utilizing 4th order Runge-Kuta method.

where

- x_1 = the fractional conversion of total sulfur
- x_{1m} = the fractional conversion of total sulfur at steady state
- x_2 = the fractional sulfur dioxide formed
- x_3 = the fractional calcium sulfate formed
- x_{3m} = the fractional calcium sulfate formed at steady state
- x_4 = the fractional calcined limestone (CaO) formed

A, B, C = the parameters related to the physical properties of given particles and concentration of O_2

D_1 = a structural parameter includes the effective diffusivity of O_2 in ash product layer in coal fine particles

D_2 = a structural parameter includes the effective diffusivity of SO_2 in the product layer of limestone particles

K_1 = a kinetic parameter includes the rate constant of SO_2 formation

K_2 = a kinetic parameter includes the rate constant of calcium sulfate formation

RESULTS AND DISCUSSION

The effect of O_2 flowrate on the sulfur fixation rate was examined. The result showed that if the air flow rate was above 1.8 l/min, there was no effect on the rate of sulfur fixation. This indicates a negligible resistance to gas film diffusion above the flowrate of 1.8 l/min. The internal mass transfer in the agglomerate was also examined by varying the agglomerate sizes. The experimental results indicated that if the agglomerate size of less than 3/8-in. diameter were used, the SO_2 - O_2 -CaO reaction could be studied in the absence of pore diffusion resistance in the agglomerates. The reaction order for the SO_2 and limestone system was analyzed by varying the amount of limestone addition. Seventy percent of sulfur retention can be achieved at Ca/S mole ratio of 3 or higher. The correlation of initial rate and the concentration of limestone showed that the reaction was first order with respect to the concentration of limestone in the agglomerates. The calcination of limestone in the agglomerate was described by a diffusion model. Assumed that the calcination was controlled by the diffusion and the kinetic effect was negligible. Several coal fine agglomerates without limestone addition were also tested to determine the effect of CaO in the coal ash and the net effect of limestone addition on

the rate of sulfur fixation. The representative results of these studies are shown in Fig.4. The kinetic and structural parameters in the rate expressions were obtained for the given experimental conditions, and determined by trial and error as the one that best fit the experimental data. The comparison of predicted and observed values are depicted in Fig.5. Good agreement between predicted and observed experimental data was obtained. A slower initial rate of sulfur fixation was noted, which could attribute to the time required for calcination of limestone and evolution of SO_2 from the surface of the agglomerates. An enhancement of the combustion rate in the presence of limestone was also detected. Drastic changes in the structure of the agglomerates can be predicted as temperature increase through the structure parameters in the kinetic models. The rate constant for the overall sulfur fixation obtained from experimental data can be expressed as follows.

$$k_i = 21.0667 \text{ Exp}(-7,300/RT) \quad \text{for } 500-700^\circ \text{ C} \quad 8)$$

$$K_i = 3.5057 \text{ Exp}(-3,860/R) \quad \text{for } 700-900^\circ \text{ C} \quad 9)$$

CONCLUSION

Kinetic studies are reported here on the in-situ sulfur fixation in the coal fine-limestone agglomerates during combustion. The sulfur is first oxidized to form SO_2 , while limestone is calcined to form CaO , and the intermediate gaseous product, SO_2 , subsequently reacts with calcined limestone and oxygen to form calcium sulfate. Diffusion is found to play an important role in sulfur fixation rate. The unusually low activation energy found for the sulfur fixation reaction is thought to be due to the time requirement for limestone calcination and emission of SO_2 from the surface of the agglomerates at initial stage. The sulfur fixation rate data have been interpreted based on a coupled diffusion and zone-reaction model, and the kinetic and structural parameters obtained for the temperature ranges of $500^\circ - 900^\circ \text{C}$.

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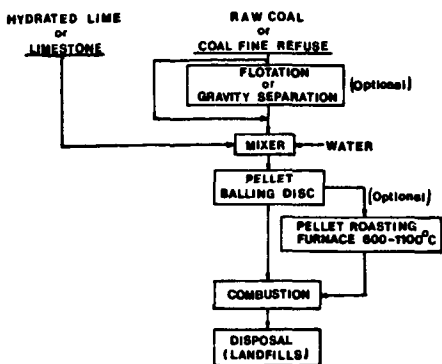


FIG.1 FLOWSHEET FOR COAL FINE REFUSE-LIMESTONE COMBUSTION PROCESS

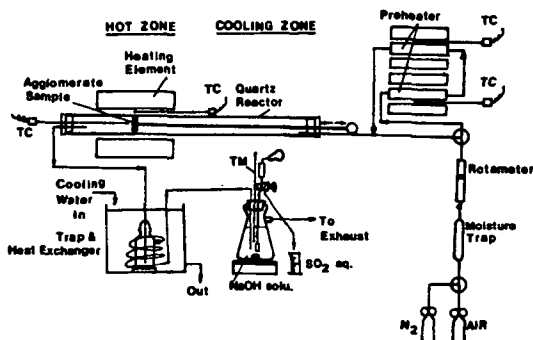
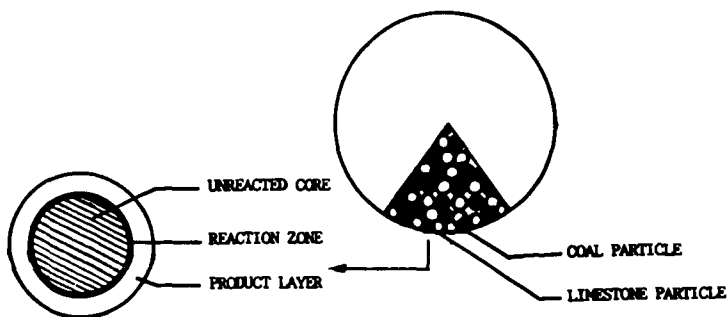


FIG.2 SCHEMATIC DIAGRAM OF COMBUSTION SYSTEM FOR COAL FINE REFUSE-LIMESTONE AGGLOMERATE



zone Reaction Model

FIG.3 A COUPLED DIFFUSION-ZONE REACTION MODEL

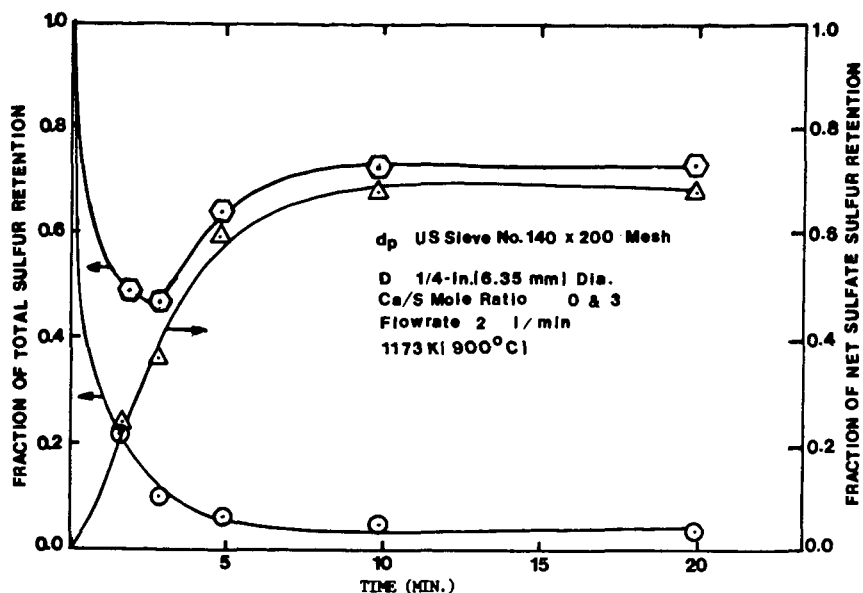


FIG. 4 THE RATES OF SUCCESSIVE SULFUR FIXATION REACTIONS - FRACTIONAL TOTAL SULFUR RETAINED AND FRACTIONAL SULFATE SULFUR RETAINED IN THE 1/4-in. (6.35mm) COAL FINE AGGLOMERATE IN THE PRESENCE/ABSENCE OF LIMESTONE AT 1173K (900 DEG. C) AND 1 ATMOSPHERE

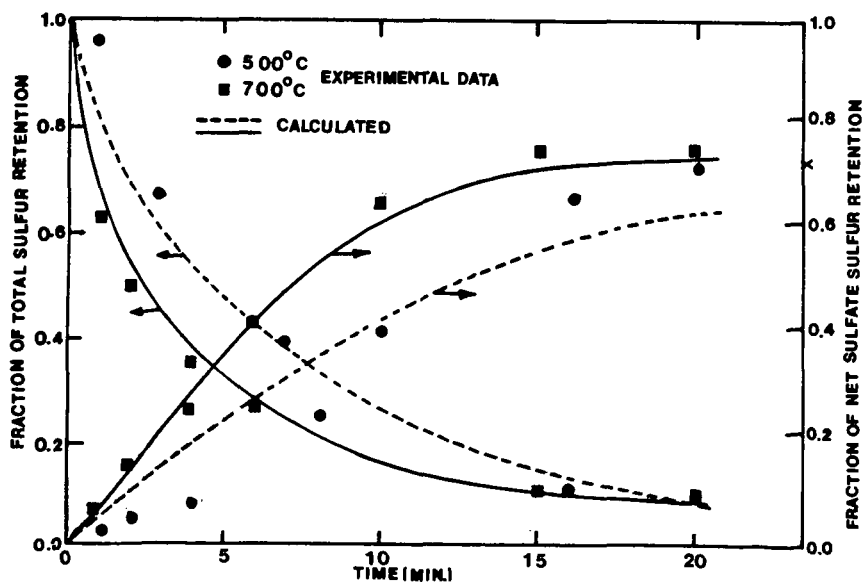


FIG. 5 Comparison of the Calculated Curves with Experimental Data for the Sulfur Fixation in the Coal Fine-Limestone Agglomerates